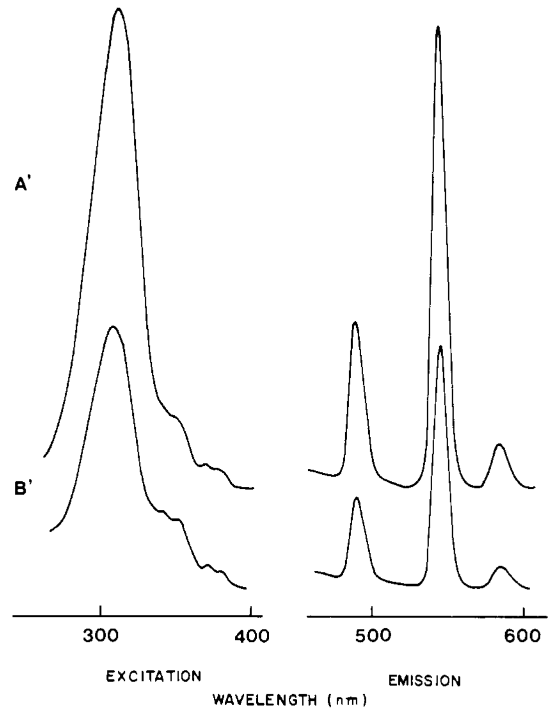
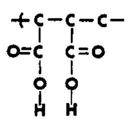
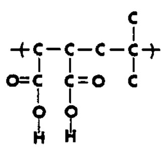


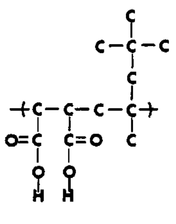
Figure 4. Effect of ultrasonic irradiation on excitation spectra (left) and emission spectra (right) of Tb^{3+} ion in maleic acid–ethylene copolymer. The copolymers MA–E, MA–*i*-Bu, MA–3-MePe were obtained from Monsanto Chemical Co. and their molecular weights were about 100 000. (A′) After 20 min of ultrasonic irradiation, (B′) before ultrasonic irradiation. [COOH] = 5.0×10^{-2} M, [Tb^{3+}] = 1.0×10^{-3} M, and pH ~9.0.

PMA–Tb^{3+} system with ultrasonic radiation produced no change in fluorescence intensity since the corrdination structure of the Tb^{3+} with the carboxylates did not change.

In order to further verify the ultrasonic irradiation effects on the Tb^{3+} ion binding to polyelectrolytes, the fluorescence properties of Tb^{3+} salts of three 1:1 maleic acid–olefin copolymers were investigated. The 1:1 copolymers were maleic acid–ethylene (MA–E) **1**, maleic acid–isobutene (MA–*i*-Bu) **2**, and maleic acid–2,3,3-trimethyl-1-pentene (MA–3-MePe) **3**.


1 MA-E


2 MA-iBu


3 MA-3MePe

The absorption peak and fluorescence intensity were also found to be greatly increased when Tb^{3+} ions were bound to these copolymers. When solutions of the Tb^{3+}–(MA–E) and Tb^{3+}–(MA–*i*-Bu) systems were irradiated with ultrasonic radiation, the absorption peak and fluorescence intensity were enhanced as found in the Tb^{3+}–PAA system (Figure 4). However, in the case of the Tb^{3+}–(MA–3-MePe) system, neither the absorption nor the fluorescence intensity changed under ultrasonic irradiation. This is believed to be due to the limited flexibility of the chain caused by the bulky methylpentane group. As a result, the coordination structure between Tb^{3+} and carboxylate would not be expected to change under ultrasonic irradiation.

The results reported in this communication show that the coordination structure of flexible synthetic polyelectrolyte salts in aqueous solution rearranges on ultrasonic irradiation. The rare earth ion fluorescence probe technique has been shown to be useful for the elucidation of such structural changes. Multiple experiments along the lines described here are in progress and will be described at a later date.

Acknowledgment. We thank Professor H. Morawetz for helpful discussions.

References and Notes

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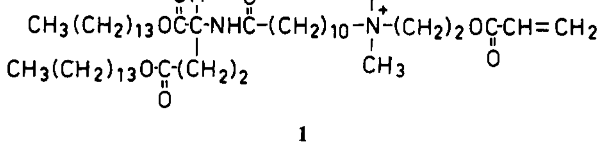
Ordered Cast Films of Polymerized Bilayer Membranes

We describe herein the preparation of highly ordered bilayer films by casting of aqueous dispersions of polymerized bilayer membranes.

It has been shown that a large variety of synthetic amphiphiles undergo spontaneous assemblage to stable bilayer membranes which display physicochemical characteristics similar to those of biolipid bilayers.[1] These aqueous bilayers are often not stable enough to use as functional vesicles, and there are inherent inconveniences in the aqueous bilayer dispersion. These disadvantages have been remedied by two lines of approach: one is polymerized vesicles,[2–6] which are a current target of active investigations for obtaining stable vesicles, and the other technique is immobilization,[7–20] which rendered possible to use bilayers as macroscopic films. The results described in this paper open a new branch in this field by combination of these two approaches.

Amphiphile 1[21] gives by sonication in water colloidal dispersions which are shown by electron microscopy to contain vesicles and lamellae of bilayers. The crystal-to-liquid crystal phase transition temperature, T_c, of the aqueous bilayer was determined to be 42 °C by differential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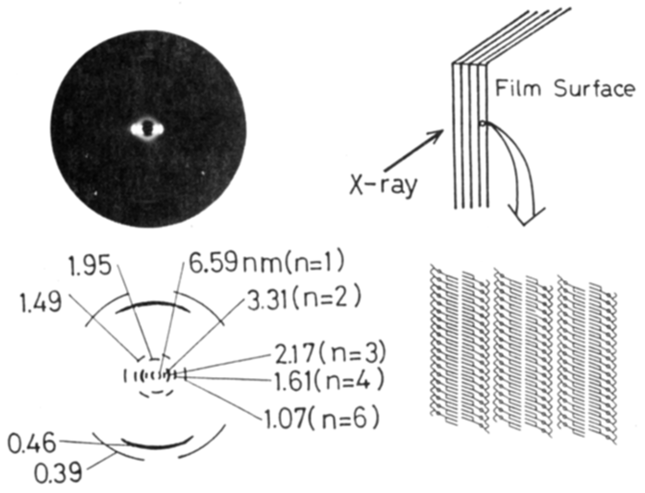

Figure 1. Wide-angle X-ray diffraction and a schematic illustration of a cast film of the polymerized bilayer of 1. Polymerization was conducted in water at 30 °C by irradiation with a 500-W high-pressure Hg lamp (Ushio UI-501C) for 10 min. The propagation of the polymer chain is not necessarily restricted to each half-bilayer.

scanning calorimetry.[22] The dispersion (20 mM) was placed in a quartz Thunberg tube, flushed with N_2 for 30 min, and irradiated at given temperatures with a high-pressure Hg lamp for 10 min. Completion of polymerization was confirmed by disappearance of vinyl protons (NMR) in the polymers, which were dried and redissolved in $CDCl_3$. The molecular weights of the polymers measured in chloroform by the light scattering technique[1] were 10^5–10^6. The aqueous solutions remained transparent after polymerization, and electron microscopy indicated preservation of the original aggregate morphologies. The T_c values of the polymerized aqueous bilayers (40 ± 1 °C), though slightly affected by the polymerization conditions are quite close to that of the unpolymerized bilayer (42 °C) and suggest that polymerization proceeds without significantly disturbing the bilayer structure. Regen et al.[3] reached a similar conclusion in the polymerization of acrylated lecithins.

The polymerized dispersions in water were spread on siliconized glass dishes and allowed to stand for 2–3 days at 15–20 °C. Transparent, self-supporting films (thickness, ca. 10 μm) were obtained by this casting procedure. The existence of the phase transition in the cast films (T_c = 47 °C) clearly shows that the bilayer assemblage is preserved. The T_c enhancement upon casting has been observed in other systems.[10,12–14]

Figure 1 displays a wide-angle X-ray diffraction pattern (instrument: Rigaku Denki Rotaflex R-200, Cu Kα) of cast polymer film. The X-ray beam was irradiated parallel to the film plane, which was set vertically (edge view). The equatorial diffraction is observed up to the sixth order with a long spacing of 6.59 nm. This suggests that regular molecular layers exist normal to the film plane. The axial diffractions indicate that some extent of molecular orientation is also maintained in the direction parallel to the film plane. It is surprising that simple casting of the polymerized bilayer produces a self-supporting film with a highly ordered structure. The polymerization temperature is decisive in preparing the highly ordered film. A cast film of the polymerized bilayer gave only Debye–Scherrer rings (long spacing, 7.23 nm) in X-ray diffraction when polymerization was conducted at 50 °C ($T > T_c$). This indicates that macroscopic ordering is not maintained in spite of the presence of the bilayer structure (T_c = 47 °C).

In conclusion, highly ordered bilayer films are obtained by casting of polymerized bilayer dispersions. Macroscopic ordering supposedly starts at the air–water interface and grows from the surface down. The probable randomness in the conformation and stereochemistry of the polymer main chain does not interfere with macroscopic ordering of bilayers. The cast film combines covalent stability of polymers and molecular orientation of bilayers and should be interesting as a new class of organic solids. Detailed investigations are in progress concerning influences of the chemical structure and the physical state of the component bilayer on the macroscopic ordering.

Registry No. 1, 96502-32-8; 1 (homopolymer), 96502-33-9.

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